

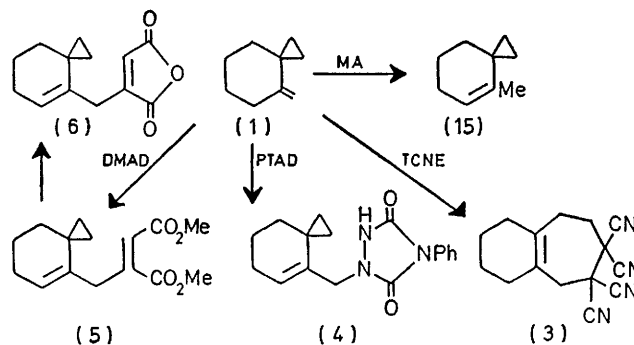
Alternative Modes of Addition of Dienophiles to Vinylcyclopropane Systems

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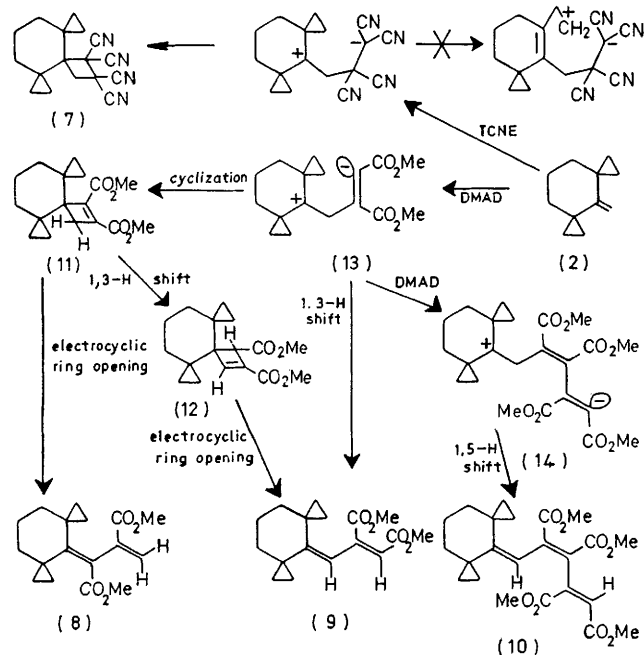
Summary Two alternative modes of addition to vinylcyclopropane systems are here described for each of two dienophiles: tetracyanoethylene is shown to react either via [2 + 2] or by [2 + 4] cycloadditions; and dimethyl acetylenedicarboxylate reacts either by the "ene" route or by way of insertion to the double bond.

THERE are a few examples of $[\pi 2 + \pi 2 + \sigma 2]$ cycloadditions involving 1,5-conjugative additions of dienophiles to vinylcyclopropanes to form the corresponding 7-membered ring-systems. The recorded reactions involve additions to α -cyclopropylstyrene,¹ *N*-methoxycarbonyl-2,3-homo-pyrrole,² bicyclo[2,1,0]pent-2-ene³ and *trans*-2-phenylisopropenylcyclopropane.⁴ The dienophiles used in these re-



SCHEME 1

actions include maleic anhydride (MA),¹ *N*-phenylmaleimide,² dimethyl acetylenedicarboxylate (DMAD),² tetracyanoethylene (TCNE)³ and chlorosulphonylisocyanate.⁴ It is



SCHEME 2

peculiar that highly reactive dienophiles such as 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD),⁴ or benzyne,⁵ do not add across the vinylcyclopropane systems, and react instead

ated by g.l.c. to provide a $C_{15}H_{14}N_2$ product (m/e 250), shown to result from a "homodienic synthesis," in the sense that two π bonds and one σ bond were converted into two new σ bonds and one π bond with the formation of a 7-membered ring [(3) Scheme 1]. The disappearance of both cyclopropane and vinylic signals in the n.m.r. spectrum of (3) is in line with the structure assigned.

Addition of equimolar quantity of PTAD to a solution of (1) in acetone at room temp. (3.5 h) did not produce a 7-membered ring, but led instead to an "ene" reaction product, (4), as inferred from its n.m.r. spectrum, its i.r. absorption at 3170 cm^{-1} (N-H), and its mass spectrum displaying a molecular ion peak at m/e 297 and a base peak at m/e 79, which arise from successive losses of neutral species of PhNCO, HNCO, and two ethylene molecules.

A similar "ene" product, (5), was obtained by heating a two molar excess of DMAD with (1) for 20 h in a sealed tube. It was cyclized in a two-stage process into the corresponding anhydride, (6) (i.r.: 1845 and 1780 cm^{-1}).

Unlike (1), the "ene" reaction in (2) is precluded due to absence of allylic hydrogens, which in turn should increase the probability of the $[\pi 2 + \pi 2 + \sigma 2]$ cycloaddition. However, the reaction of equimolar quantities of (2) and TCNE yielded within a few minutes the 1:1 [2 + 2] cycloadduct (7) (Scheme 2). The preference of the [2 + 2] addition over that of 1,5-addition is manifested also by the emergence of (8) and (9) from the reaction of a 3-fold excess of DMAD with (2) (48 h, 120°). The immediate precursors of (8) and (9) are, presumably, the corresponding cyclobutene intermediates, which are the sole cycloproducts of this reaction. They arise from the collapse of the dipolar intermediate⁸ (13), first to (11), and then to (12), via a 1,3-hydrogen shift. The main product of this reaction is, however, the 2:1-adduct, (10), (m/e 432). This clearly

TABLE

Compound	(3)	(4)	(7)	(8)	(9)	(10)
M.p., °C	94	124	181	58	63	106–108
λ_{\max}/nm (log ϵ)	—	—	—	210(4.00) ^b 250(3.48) ^b	210(4.00) ^b 300(3.60)	208(4.02) ^c 227(3.38) 310(3.38)
τ (cyclopropyl) ^a	—	9.33	9.8–8.7	9.8–9.1	9.7–9.1	10.0–9.0

^a 60 MHz in CCl_4 . ^b In EtOH; ^c In C_6H_{14} .

either by the "ene" route or by way of [2 + 2] cycloaddition.^{4,5} We report a new case of a "homodienic" synthesis and a new insertion reaction in two new vinylcyclopropane systems.

The hydrocarbons (1) and (2) were synthesized from the corresponding ketones,⁶ by application of a modified Wittig reaction.⁷ They show molecular ions at m/e 122 and 148, respectively, in the mass spectrum.

An excess of (1) was allowed to react with TCNE for 4 h at room temp. in MeCN under N_2 , and the mixture separ-

indicates that system (2) has no tendency to react with DMAD in either mode of cycloaddition, but rather reacts via chain insertion, yielding the trienic product.

The structures of (8)–(10) were based on their spectroscopic data and the oxidative degradation of their side-chains, to provide the known dispiro[2,1,2,3]decan-4-one.⁶

Finally, both (1) and (2) failed to add maleic anhydride. (1) isomerized into (15) on heating with MA (24 h).

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